

Poster #204

LLNL Scientific Focus Area – Subsurface Biogeochemistry of Actinides

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The objective of LLNL's SFA is to *identify and quantify the biogeochemical processes that control the fate and transport of actinides in the environment*. The research approach combines three Thrusts: (1) **Fundamental Mechanistic Studies** that identify and quantify biogeochemical processes, (2) **Field Integration Studies** that investigate the transport characteristics of Pu in the environment, and (3) **Actinide Research Capabilities** that provide new opportunities for advancing actinide environmental chemistry.

Research Thrusts 1 and 2 are guided by broad central hypotheses:

***Thrust 1 Hypothesis:** The biogeochemical mechanisms controlling **redox transformations of actinides and their stabilization** as aqueous complexes, binary surface complexes, ternary surface complexes, precipitates, and co-precipitates will determine actinide migration in the environment.*

***Thrust 2 Hypothesis:** The biogeochemical processes that ultimately control actinide subsurface mobility/immobility are driven by local variations in the geology, geochemical conditions, colloid composition and abundance, and **chemical characteristics of the initial actinide source**.*

Research Thrust 3 is not hypothesis driven. Instead, it is guided by the research efforts and capability development needs described in Research Thrusts 1 and 2.

Here, we summarize the accomplishments from 2016 that span all three Thrusts. Pu(IV) and Pu(V) sorption to goethite at sub-femtomolar to micromolar concentrations revealed how concentration affects redox transformation rates and formation of surface precipitates. The effect of natural organic matter on Pu sorption to goethite was examined to identify solution conditions that lead to formation of ternary surface complexes. The interactions of Pu with *Pseudomonas* sp. Strain EPS-1W and its extracellular polymeric substances was investigated to determine the role of microbes in Pu transport. Desorption rates of plutonium from montmorillonite colloids was investigated to determine the extent of colloid-facilitated transport at environmentally relevant timescales. Colloid-facilitated transport experiments of Th(IV) with hematite ($\alpha\text{-Fe}_2\text{O}_3$) colloids and Suwannee River fulvic acid were performed to examine ternary colloid transport rates. Long-term (~6 year) diffusion of U(VI) through bentonite was investigated and revealed much slower migration behavior than observed in short-term experiments. The pressure dependence of carbonate exchange with $[\text{NpO}_2(\text{CO}_3)_3]^{4-}$ in aqueous solutions was studied to quantify molecular scale rate-limiting processes and revealed that f-electrons affect ligand exchange mechanisms and rates. A novel solid-state NMR method for the investigation of trivalent lanthanide sorption on amorphous silica at low surface loadings was developed for use in actinide mineral-water interface studies. Finally, a review paper entitled "Behavior of plutonium in the environment" was published together with our Russian collaborators in a special issue of Russian Chemical Reviews devoted to the Boris Myasoedov 85th anniversary. This work was supported by the Subsurface Biogeochemical Research Program of the U.S. Department of Energy's Office of Biological and Environmental Research.